

ASSESSMENT OF CASTING BINDING MATERIALS BASED ON MODIFIED TECHNICAL LIGNOSULFONATES

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ABSTRACT

This study examined the efficiency of employing technical lignosulfonates (TLS) - compositions in developing foundry binder materials that comply with the modern requirements for a casting production. Modifying TLS through a non-ionic surface-active substance (SAS), with the samples of neonol were used, and then investigated, as its action removes the disadvantages of insufficient strength properties. In comparison with the currently used synthetic resins, the new TLS-based binders possess high strength characteristics. Biopolymer binders based on TLS are superior to synthetic resins now in use, mainly in terms of labor safety, production ecology, and process economics, with the cost of TLS is 0.07-0.094 \$ / kg, while the cost of the resin is 3.8-5.5 \$ / kg. TLS is made from domestic plant materials, which is a renewable resource that can provide the required needs of foundry production. The disposal of the core and molding mixture containing binders modified with the TLS is eco-friendly; it uses a biopolymer base that is easily degradable in the natural environment. Moreover, the developed form does not produce toxins, which are phenolic-based synthetic resins obtained from the casting production.

KEYWORDS: Lignin, Technical Lignosulfonates, Binding Ability, Modification, Foundry Binders, Surfactants, Neonol, Synthetic Resins & Castings

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INTRODUCTION

Binding Materials

Binding materials governs the modern look of the foundry, this can be attributed to the fact that they are the basic structural components that serve as the quality indicators of the mold, on which the quality of the casting depends. The role of foundry in the total output in economy's various sectors is seen as an indicative: in the automotive industry ranges from 8–10%, in tractor engineering 15–18%, in agricultural machinery 15–20%, and in the engine industry the share of casting dominates by reaching 70 –80%, while these indicators are steadily increasing [1]

An illustrative indicator is the production of castings in the countries with the highest industrial outputs. For example, the researcher in a previous study expected that the USA in 2018, this indicator in value terms would reach \$ 33 billion, with a prediction of an increase in the production by 4.7% in 2017–2018 and 1.8% in 2018-2019[2]. A similar trend was observed in Germany [3].

The above is also accompanied by an increase in requirements for the quality of castings[1, 4], the complexity of their design, and strict environmental standards[5].

Over the earlier 30 years, tolerances and allowances for castings have been minimized by 1.5–2.0 times, the metal consumption of castings has shrink by 10–20% [1], in many scenarios, this may reach 30% [3], which is

achieved by employing a variety of innovative methods namely. the molding of composite materials.

Further improvement of the foundry industry, necessitates new peremptory norms for technological processes, including the creation of effective technologies, to be safe at the same time, based on accumulated practical experience as well as modern scientific ideas about the physicochemical phenomena occurring in the production process, along with the integration of innovative developments in the related fields such as implementation of the different energy types in such production process and using a different type of engineering simulations [6–38].

OBJECTIVES

This study aimed to develop a new binder material based on a biopolymer substance that guarantees the strength requirements, in addition to ensure the quality of casting wherever the technical lignosulfonates are used as the feedstock of biopolymer-based materials.

ANALYSIS AND DISCUSSION

Currently the pressing problem is the technical efficiency for manufacturing high-quality castings at a minimal cost with an acceptable level of emissions that ensures workplace safety and minimizes foundry's environment footprint.

What distinguishes casting technology is the use of casting cores, which forms the inner surface of the body of the casting during its production. These components are composed of single sand mixtures, composite materials with quartz sand is used as a filler, and as it is well-known resin materials are used as a binder. Foundry core is considered as the dominant factor that determines the quality of future castings. However, the indicators that determines quality, notably are dimensional accuracy, surface cleanliness, the presence of gas sinks and sieve porosity in the body of the casting, among others.

The influence of rods on quality is invariably emphasized in various scientific publications throughout the foundry development period, which has become the subject of scientific research, both in its early period [39, 40] and now [4, 41], with special attention to the safety issues[42].

Employing purge technologies ensures the technological efficiency of the production of foundry cores, thus, combining the process productivity with high quality. A good example here is the Cold-Box Amin process [1, 43]. Despite, its total dominance in the modern foundry, as proved in [44-46], making castings for rocket engines using this technology [47] is disadvantageous. Castings content compromises of two points:

Firstly, the high cost of the initial binders used in the process. This indicator can vary between 3.5 - 5.0 euros / kg per binder (approximately \$4-6/ kg), and more, to ensure the special requirements for strength, collapsibility and etc., while the price of lignosulfonates is approximately \$ 0.07 – 0.09 / kg.

Secondly, the usage is dangerous, both for workers at the foundry and the surrounding area of the enterprise, which is linked to the nature of the binder composition used in the process.

The binding system includes three components: component **A** - phenolic resin - substances of the first and second hazard classes; component **B** - polyisocyanates - substances of the first hazard class (sodium cyanide and potassium cyanide can be attributed to the homologous series of these substances); and the third **is**, component **C**, the gaseous catalyst - tertiary amines, which are carcinogens that belongs to the first hazard class.

The toxicology of the catalysts used in the Cold-Box Amin process reveals that amines are very toxic substances, as inhaling their fumes and direct contact with the skin is harmful. Amines, for example, aniline can be absorbed through the skin into the bloodstream and disrupt hemoglobin functions, which can lead to fatalities.

Symptoms such as blueness of the fingertips, nose, lips, shortness of breath, rapid breathing and palpitations, as well as loss of consciousness are associated with the amine blood poisoning[47].

Aliphatic amines, which are used in this process, affect the nervous system that may cause violations of the permeability to the walls of blood vessels and cell membranes, liver functions and the development of dystrophy.

Aromatic amines lead to the formation of methemoglobin, which inhibits the central nervous system. A number of aromatic amines are carcinogens; they cause bladder cancer in living tissues[48]. Regular long-term exposure, even with small doses, amines can cause harm to the human body, including allergic diseases, chronic asthma, and a tendency to tumor diseases[47].

Cold-Box Amin is considered as the main process in the production of small and medium rods during the manufacturing of castings; this can be attributed to the advanced equipment and gained experience in the field of castings manufacturing. As a matter of fact, the modern requirements for the safety of production processes adopted in the countries of the European Union [5] nictitate looking for a relevant alternatives.

These studies include the use of lignin-containing binder materials, such as technical lignosulfonates (TLS). Similar technical solutions were reached in [49], and provided describing the corresponding technological equipment, for example, in [50], a process similar to Cold-Box Amin has been created. In this regard, it is advisable to conduct adaptive search experiments to consider the fundamental possibility of such technical solutions.

The use of lignin materials is environmental friendly in terms of safety, both in terms of the suggested future developments [51] and in the class of lignin-containing substances as a whole [52, 53].

Built on the profound experience of experimenting TLS as a binder in the foundry, with taking into consideration about the existing scientific developments, this study focused on the effect on TLS with a numerous chemical modifiers (modification) from the surfactant class SAS.

Technical liquid and powder lignosulfonates are by-products of wood processing. TLS are made from a mixture of lignosulfonate acid salts that combined with reducing and mineral substances, obtained from liquors of the bisulfite pulping. The quality indicators of TLS are shown in the table 1.

Table 1: Technical Lignosulfonates				
No.	The Name of Indicators	Tls	Modified Tls	Powder Tls
1	Mass fraction of solids,%, not less	47	92 (powder) 53 (liquid)	
2	PH of an aqueous solution, not less	4,4	4,4	4,5
3	Tensile strength of dried samples, MPa, not less than	0,6	0,6	0,69
4	Humidity,%, no more	–	-	4,0
5	Mass fraction of ash to the mass of dry substances,%, no more	18	22,0	18,0
6	Conventional viscosity, s	50-320	50-320	-

7	Mass fraction of reducing substances to the mass of dry substances, %, no more	–	15	10
8	Density, kg / m ³ , not less	1230	1260	–

To insure the secure requirements, TSL are powdery - combustible, fire and explosion-proof, bestow to the extent of exposure to the body, that liable to substances of the 4th hazard class (inert, not dangerous to humans).

In the foundry, they are used in the liquid state: TLS grades “A” and “C”. The first is for foundry and the second for general technical purposes. TLS as a casting binder is regarded as an aqueous solution of lignosulfonic acids with a sodium, calcium or ammonium base, which has a dark brown color, with slightly a specific smell.

Liquid technical lignosulfonates were emptied into railway tanks with bottom discharge, barrels and tankers among others. Powdered technical lignosulfonates were put in paper and polypropylene bags, as well as in soft, specialized, disposable containers.

Special conditions were applied to the transportation of powdered technical lignosulfonates to prevent product wetting, as it can be transported by rail, road and water. To reach consumers, soft specialized containers can be dispatched by railroad cars, gondola cars or by road, that to be delivered to consumers.

To prevent product moisture, TLS are stored in closed ventilated warehouse. However, in winter, the condition of liquid lignosulfonates thickening, they are heated in a tank with dead steam, i.e. with coil made of acid-resistant steel, lowered into the tank through the upper hatch. They assure shelf life of the liquid fraction of TLS in a closed container, at a moderate temperature for one year from the date of its production. Their application suggests much longer periods of conservation while retaining, the key quality characteristics (in case of thickening, during long-term storage, add water, carry the necessary density and apply as intended). The shelf life of a bagged dry portion in a dry room is for 1 year at a temperature that does not exceed 40° C.

Technical Lignosulfonates are Used

- As a diluent for the raw mix to reduce sludge moisture in the manufacture of cement;
- As a binder in the production of molding and core mixtures in iron, steel, and non-ferrous castings;
- During agglomeration of ferrous metal ores; in the manufacture of refractories; when briquetting;
- As lubricating and cutting fluids during hot stamping and forging;
- As a foaming agent for acid etching of a metal;
- As a sizing agent for cellulose-containing substrates in the textile industry;
- As a plasticizing material in the manufacture of drywall sheets;
- During the granulation of carbon black and porous fillers from bulk powder materials, blends;
- As a dispersant and stabilizer of suspensions in the production of chemical plant protection products;
- As lubricants and cutting fluids in hot stamping and forging;
- As a feedstock and dispersant in the manufacture of synthetic tanning agents;

- For the manufacture of chipboards, fiberboards, and plywood;
- As a plasticizer of cement and concrete;
- As a reagent for regulating the main parameters of drilling fluids for oil and gas wells;
- As a reagent for ore flotation;
- Indifferent quality in various areas of production.

This study examined the effect of non-ionic surfactants (nonionic surfactants) on the molecular mass of TLS, i.e. to modify the polydisperse composition of lignosulfonate. Accordingly, this study was carried out by a chromatographic method. It was observed that the model compositions of binder compositions with TLS of various pulp and paper mill was taken as the object of the study, and the amount of modifier in TLS was optimal - 1.3%. The results are shown in the table.

2.

Table 2: The Effect of Neonol on the Molecular Weight Distribution of TLS and their Binding Ability						
The Average Molecular Weight of the Fraction Mz, Unified unit of Mass	Content Fraction, %					
	Cellulose and Paper Mill (1)		Cellulose and Paper Mill(2)		Cellulose and Paper Mill (3)	
	TLS	TLS Nonionic Surfactants	TLS	TLS Nonionic Surfactants	TLS	TLS Nonionic Surfactants
till 300	3	3	5	4	4	4
300 – 2 000	11	5	7	4	9	4
2 000 – 5 000	25	9	41	11	46	11
5 000 – 10 000	41	63	35	69	21	60
10 000 – 150 000	20	20	12	12	21	21
Strength, MPa	0,61	2,81	0,37	3,00	0,22	2,91

It was observed that the treatment of TLS with the neonol modifier allows the polydisperse structure of TLS to be homogenized, this can be attributed to the accumulation of the fraction with numerical values of the molecular weight that range from 2000 to 5000 uum, as well as the rapid increase in the average molecular fraction with a range of values between 5000 and 10000 uum. For the effective role of non-ionic surfactant (neonol) modifiers, it is advisable to evaluate the effect of homogenization on the binding ability of TLS.

This study also examined the effect of the neonol modifier on molecular weight, wettability, and adhesive, see (figure 1.).

Cryoscopy methods were employed to study the molecular weight, while wettability was determined by changing the wetting angle through the “drop” method, and adhesion forces were identified by the original method, namely the standard tensile strength test equipment.

The device designated to measure the adhesive forces of the binder compositions consists of two round metal disks attached to the grippers on the outside to be used in a strength measuring device, and a quartz plate is attached to the inside. It simulates the interaction of the binder composition of the modified TLS with the grains of quartz sand - filler core mixture.

A 3-gm. binder composition was added to the plate, with carefully connecting the two parts of the device, so, that a uniform surface of the binder film was formed between the quartz sheets. The sample was dried for 15 minutes through

clamping it with a bracket along the boundary surfaces and keeping it in an oven at a temperature of 160-180 ° C. After cooling, the strength of rod mixtures was tested.

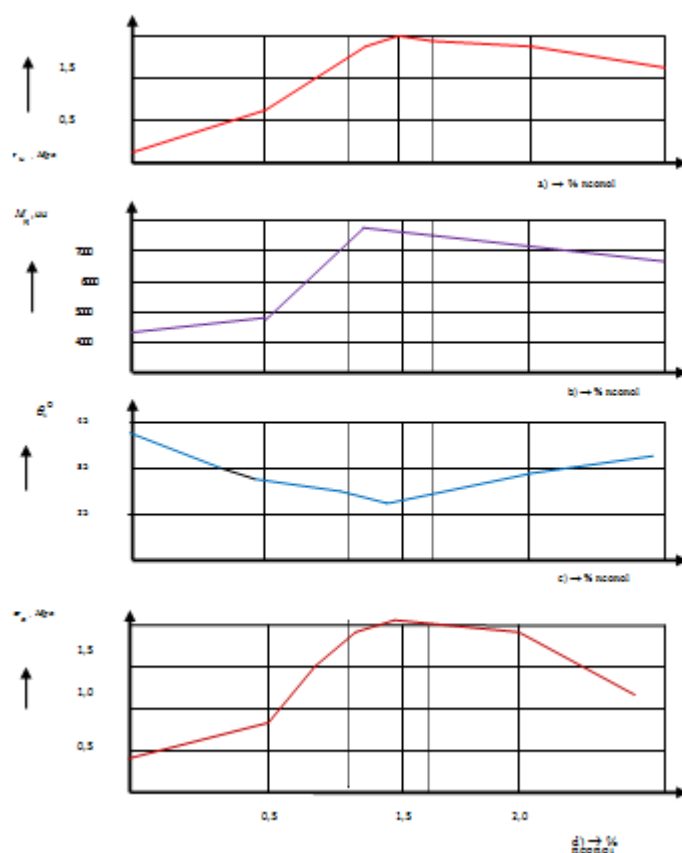


Figure 1: A Comprehensive Study of the Influence of the Non-Ionic Surfactant Modifier on: the Change in the Physicochemical Properties of TLS: a) The Binding Ability; b) Molecular Weight; c) The Contact Angle; d) The Adhesive Forces.

Due to the formation of donor-acceptor cooperative bonds, the chemical reaction proceeds with the formation of a three-dimensional polymer network and acquire the structure shown in Fig. 2. In fact, this predetermines an improvement in the binding potential of TLS, which opens the possibility of synthesis based on the new modern biopolymer-based foundry binders.

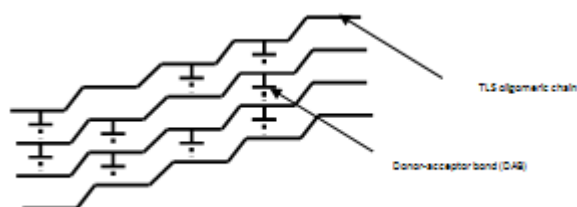


Figure 2: A Simplified Diagram of the Structure of a Three-Dimensional Network Polymer of a Binder Composition, Formed as a Result of Thermal Curing on the Basis of TLS – NSA Nonionic Surfactants (Neonol).

RESULTS AND DISCUSSIONS

This study focused on tangible results, including the effect of the Neonol modifier on TLS, and the changes in the physical-chemical properties of the binder compositions based on TSL.

This study showed that the structure of the molecular weight distribution is equalized (the polydispersity of the composition is low) while the molecular weight grows, as a result of micellization process in the volume of the binder fluid.

It was also observed that wettability increases as a result of a decrease in the wetting angle by 21 - 25%; the stresses in the films of the composition of binder on the surface of the filler fall down.

Due to changes in the structure of TLS, as well as the aggregation of TLS in the colloidal state, the adhesive strength increases up, while the stresses in the films and cuffs fall down.

As a result of this, a three-dimensional network polymer was formed due to the occurrence of a chemical interaction between the oligomeric TLS chains and the Neonol modifier introduced into the composition, which is manifest in the final strength parameters of the binder.

CONCLUSIONS

Biopolymer compositions based on the technical lignosulfonates (TLS) proved its efficiency in developing foundry binder materials that comply with the modern requirements for casting production.

TLS were modified by non-ionic surface-active substances (SAS), with neonol was chosen as an example that have eliminated the drawbacks of insufficient strength properties.

In comparison with the synthetic resins, that also distinguishes TLS-based binders is the high strength characteristics. TLS-based binders are superior to synthetic resins in terms of labor safety, production ecology and process economics (TLS costs 0.07-0.094 \$ / kg, the cost of resin is 3.8-5.5 \$ / kg).

Moreover, TLS are domestic-made materials produced from natural resources like plant materials, which is a renewable resource; accordingly, the resource base can address the needs of foundry production.

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AUTHOR'S PROFILE



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Research Interests: binding materials for casting processes; theoretical foundations of nature similarity in technology; nature-like technologies in foundry; theoretical foundations of creating algorithms for the development of new technological processes based on the integrated accounting of structural factors of their development; biopolymer composite materials; implementation of environmental and economic imperatives in the production, development, and creation of environmentally friendly and economically competitive technological processes; new functional materials on a lignin-containing basis.

Developed complex technological additives to ensure the manufacturability of casting mixtures based on liquid glass, providing their facilitated softening at the stages of extraction of castings from the mold.

The author proposed to consider technical lignin as a functional material with a wide range of applications, depending on the processing depth and the selective enhancement of individual physicochemical properties of this material. A variety of possible areas of its application are theoretically substantiated, almost some of them are embodied in casting processes. The most important theoretically possible is the creation of biocomposite lignin-based super accumulator, an order of magnitude superior to modern analogs, as well as the use of sorption properties of lignin for fine purification of various liquid media.

The author of the article has 137 scientific publications at various levels, 5 patents, is a co-author of one textbook and 4 monographs.